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FUNDAMENTALS OF THE OXIDATION  
PROTECTION OF  
COLUMBIUM AND TANTALUM

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## Forword

This is the fifth semiannual report on NASA Grant No. NGR 33-013-017. It covers work from October 1, 1967 to April 1, 1968.

The first two reports were issued March 31, 1966 and October 1, 1966 and had limited distribution. The third report, accordingly contained a comprehensive review of the entire program and was issued April 1, 1967. The fourth report was issued October 1, 1967.

This grant was made by the NASA Office of Grants and Research Contracts. The NASA Technical Monitor is Mr. Robert E. Oldrieve of the Lewis Research Center, Cleveland, Ohio. The work is under the supervision of Professors Morris Kolodney and Robert A. Graff and is being performed by Mr. Stanley R. Levine, Mr. Andrew G. Mueller, Mr. Leon Schwartz and Mr. Frederic N. Schwettman who are graduate students at The City College of New York. A fifth graduate student, Mr. George Halbfinger, joined the project in December 1967.

## Summary

An investigation of the fundamental processes involved in the protection of tantalum and columbium by their silicides is in progress. The program has four parts. The first part is devoted to establishing thermochemical data for the silicides and employs an entirely solid state electrochemical cell. The second part deals with the protection of both coating and substrate by the protective glass formed during oxidation. Under certain conditions of temperature and pressure this glass does not form and the coating fails. The study of glass structure and growth is aimed at understanding the causes of failure and providing a rational basis for improving coatings. In the third part oxidation rates and the possibility of using coating modifiers to promote the formation of glassy films is to be tested. Lastly, since coating life may be limited by the formation of intermediate phases between the silicide and the substrate, these interactions are being investigated in the fourth part of the program along with the efficacy of diffusion barriers to retard intermediate phase growth.

The previous reports described the development of specimen fabrication techniques, the design and construction of equipment and preliminary tests of some of the methods to be used. Further tests and improvements in methods and apparatus are given in this report. Preliminary results on the rate of oxidation of  $\text{TiSi}_2$  between 300 and  $1200^\circ\text{C}$  are presented. New information on interphase growth in the Ta-TaSi<sub>2</sub> system has been obtained. A new line of investigation on silicide reactions has been added.

## Contents

	<u>Page</u>
Summary	ii
Introduction	1
Thermochemical Data	3
Glass Structure and Growth	11
Oxidation Rates and Coating Modifiers	16
Substrate - Coating Interaction and Barriers	19
Silicide Reaction	23
Program for Next Six-Month Period	24
Figures	26
References	27
Distribution List	28

## Introduction

Refractory metals are required for a variety of applications at elevated temperatures, particularly for air-breathing engines, because their high strength is retained under service conditions. These metals, however, suffer from a susceptibility to oxidation. Above about 1300<sup>o</sup>F oxidation rates are prohibitive, and a protective coating is required. Silicide and aluminide coatings have been most successful thus far.

The development of coatings has proceeded by largely empirical methods. While this is undoubtedly the way to obtain practical coating systems rapidly, a successful coating technology must be backed by fundamental information atmosphere-coating-substrate systems. Previous studies on the development of protective silicide coatings were reviewed in the third Semiannual Report.

The program reported here was undertaken to provide an understanding of the behavior of the coated substrate in its environment. This involves the mechanisms and rates of oxidation of the coating and the effects of modifiers as well as the mechanisms and rates of interaction of the coating with the substrate. The tantalum-silicide and columbium-silicon systems, at temperatures up to 2500<sup>o</sup>F and under oxygen pressures of one atmosphere and above, are under study.

Four major lines of investigation are in progress:

- 1) thermochemical data,
- 2) glass structure and growth,
- 3) oxidation rates and coating modifiers,
- 4) substrate-coating interaction and barriers.

To discuss the behavior of tantalum-silicon and columbium-silicon systems under oxidation requires thermochemical data for the oxides and silicides. At present the free energies of formation of the silicides of tantalum and columbium are not available.

These are being determined in the first part of the program using a solid galvanic cell at elevated temperature.

The oxidation protection of metals by silicides depends on the formation during oxidation of a glass which acts as a barrier to oxygen. The oxidation products frequently do not form a protective film. In the second line of investigation the glasses formed on oxidation are being investigated with the objective of understanding the differences between the structure of protective and nonprotective films and the processes controlling their growth. This understanding will provide a rational basis for improving the protectiveness of coatings.

The possibility of using modifiers to improve the structure of the film is being investigated in the third part of this program. Substances which form stable oxides or silicates may be expected to increase coating life and a number of these will be tested.

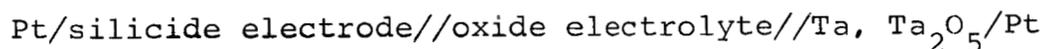
In the fourth phase of the project the interaction of the coating with the substrate is being studied. This interaction produces an intermediate silicide incapable of forming a protective film. The rate of growth of the intermediate phase may thus determine coating life. These phases grow by diffusion, and the use of barriers to slow the growth of the intermediate has been reported.

A new line of investigation, silicide reactions, has been added to support other phases of the program. Mixtures of a silicide and its oxides are examined by x-ray analysis before and after heating. Evidence of reaction, obtained in this way, gives information of thermodynamic stability.

### Thermochemical Data

Presently available thermodynamic data for tantalum and columbium silicides are limited to heats of formation obtained calorimetrically (Robins and Jenkins, 1955), by Knudsen effusion (Myers and Searcy, 1957), or by reaction equilibria (Brewer and Krikorian, 1956). The average accuracy of the best available data is about  $\pm 15\%$ . To date there have been no experimental determinations of the free energy and entropy of formation of these silicides. The free energy of formation of these compounds can only be estimated from heat of formation data under the assumption of a zero entropy of formation.

In this investigation the free energy of formation of the tantalum silicides are being determined from EMF measurements on electrochemical cells of the form:



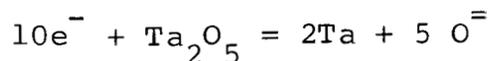
where the free energy of the reaction is given by

$$\Delta G_R = -nFE$$

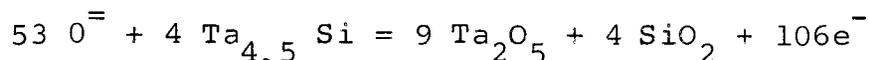
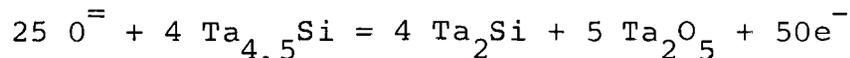
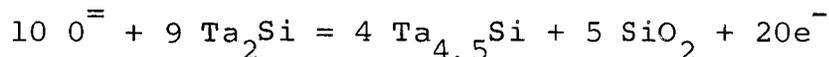
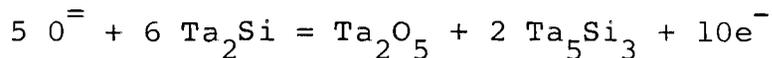
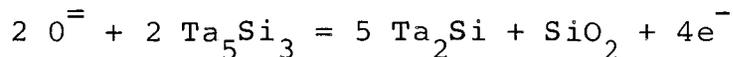
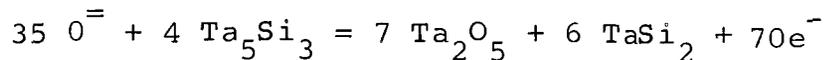
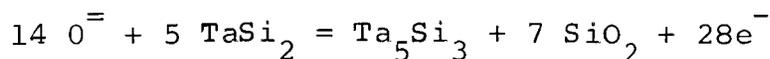
and  $\Delta G_R$  contains the known free energies of formation of  $\alpha$ -quartz and  $\beta$ - $\text{Ta}_2\text{O}_5$  and the unknown free energies of formation of the silicides. The same is true of the entropy of the cell reaction which is proportional to the temperature derivative of the voltage.

$$\Delta S_R = nF \left( \frac{dE}{dT} \right)_P$$

The reference electrode half-cell reaction may be

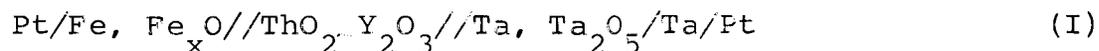


The expected reactions at the silicide electrodes, which in each case is composed of the participating reactants and products, are:



Background material on solid oxide electrolytes has previously been presented (Kolodney and Graff, 1967 b).

During the past six months a large number of cells have been examined and reproducible results, consistent with the expected electrolyte behavior, obtained for the following cell:



A number of electrolyte thicknesses and compositions were employed. Results are presented in Table I. Neither composition nor thickness was found to have a pronounced effect upon the observed voltages. However, cells 5 and 6 best followed the expected temperature dependence of EMF as can be seen by considering the small variation in the average transport number. The absence of a pronounced effect of electrolyte resistance upon cell voltage is contrary to the observation of Steele and Alcock (1965). Under null current conditions the absence of an electrolyte resistance effect can be understood by considering the diffusion of individual species in the electrochemical field.

Table I

Results For Cells of The Form Pt/Ta/Ta,Ta<sub>2</sub>O<sub>5</sub>//ThO<sub>2</sub> Y<sub>2</sub>O<sub>3</sub>//Fe,Fe<sub>x</sub>O/Pt

Cell No.	Electrolyte	Relative Resistance at 1000°C	Temperature °C	EMF (avg)	Average Transport No. $t_i$	Local Transport No. $t_{i,loc}$
1	ThO <sub>2</sub> 7.25 mol% Y <sub>2</sub> O <sub>3</sub> 88.5% dense 0.18" thick	2.3	1000	604	0.975	0.791
			900	606	0.968	0.728
			800	608	0.963	0.659
			720	596	0.936	0.463
2	ThO <sub>2</sub> 7.25 mol % Y <sub>2</sub> O <sub>3</sub> 87.5% dense 0.17" thick	2.2	1000	598	0.965	0.725
			900	600	0.958	0.662
			800	601	0.952	0.584
			700	570	0.893	0.272
3	ThO <sub>2</sub> 7.25 mol % Y <sub>2</sub> O <sub>3</sub> 0.078" thick	1	1000	598	0.965	0.725
			900	609	0.973	0.764
			800	613	0.971	0.719
			700	608	0.953	0.564
4	ThO <sub>2</sub> 3 mol % Y <sub>2</sub> O <sub>3</sub> 0.13" thick	5.3	1000	599	0.967	0.736
			900	605	0.967	0.717
			800	605	0.957	0.626
			700	598	0.938	0.465
5	ThO <sub>2</sub> 1.2 mol % Y <sub>2</sub> O <sub>3</sub> Thickness .097"	9.7	1000	595	0.961	0.694
			900	601	0.960	0.673
			800	607	0.961	0.648
			700	613	0.961	0.620
6	ThO <sub>2</sub> 7 mol % Y <sub>2</sub> O <sub>3</sub> , .2 wt % SiO <sub>2</sub> Thickness .09"	1.2	1000	599	0.967	0.736
			900	602	0.961	0.683
			800	610	0.965	0.683
			700	622	0.975	0.736

In the presence of a low resistance path in parallel with the cell (of the order of  $10^7$  ohms) electrolyte thickness and composition will play a role; they will affect the degree of polarization of the cell. The early difficulties in this investigation are believed to be partially attributable to low resistance paths in parallel with the cell. The nature of these paths has never been determined. However, they have been eliminated. Resistance measurements on the assembled apparatus under open and closed circuit conditions at  $900^\circ\text{C}$  showed that the resistance of all possible parallel paths was greater than  $10^9$  ohms.

From the data on cells of type I an average ionic transport number

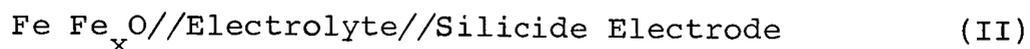
$$\bar{t}_i = \frac{E}{E^*}$$

can be calculated.  $E^*$  is the expected EMF and  $E$  is the observed EMF. Also, since the  $\text{Fe}$ ,  $\text{Fe}_x\text{O}$  electrode exerts an oxygen partial pressure which is well within the region of 100% ionic conduction for thoria-yttria electrolytes, a local transport number at the electrolyte -  $\text{Ta}$ ,  $\text{Ta}_2\text{O}_5$  interface can be calculated from the following relation:

$$t_{i_{\text{loc}}} = e^{4F(E - E^*)/nRT}$$

where  $n$  is a parameter characteristic of the electrolyte. From theory  $n$  should be 4. Steele and Alcock (1965) use a value of 2.5. The reduction in  $n$  allows for trapping of free electrons at vacant oxygen sites already present as a result of the doping with an aliovalent cation. A value of 2.5 was used for Table I.

The oxygen partial pressures over silicide electrodes will not differ appreciably from the oxygen partial pressure exerted by Ta, Ta<sub>2</sub>O<sub>5</sub>. Therefore, average transport numbers can be used to correct EMF measurements made on silicide electrodes with respect to an Fe, Fe<sub>x</sub>O reference electrode. If the voltage for the cell



exceeds the voltage for Cell I  $\bar{t}_i$  is an upper bound for the true voltage. Similarly, if the voltage of cell II is less than that of cell I  $\bar{t}_i$  as determined from cell I is a lower bound. A further check on the correction for electronic transport can be made by measuring the EMF of cells containing a Ta, Ta<sub>2</sub>O<sub>5</sub> reference electrode. In this case the sign of the voltage will indicate whether the average transport number as determined from cells of type I, is an upper or lower bound for the true average transport number. In addition, the magnitude of the voltage will give some estimate of the closeness of the bound.

A partial listing of other cells examined during the past six months is presented in Table II. There is some uncertainty about the validity of the observations because of possible low resistance paths in the system and therefore no quantitative results will be presented. Measurements on silicide electrodes which are being sintered with 0.5 wt % Ni to improve their density will be resumed and completed in the next six months.

As was mentioned in Semiannual Report No. 4, (Kolodney and Graff, 1967a) electrolytes prepared by sintering ThO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> in a vacuum furnace with Ta elements are dark green. Solutions of Y<sub>2</sub>O<sub>3</sub> in ThO<sub>2</sub> are generally brown in the presence of excess oxygen and off-white in the stoichiometric condition. Some effort is being directed at explaining these color changes. Transitions

Table II. Partial List of Cells Studied During the Report Period

Cell No.	Reference Electrode	% Theor. Density of Electrolyte to 7 mol % $Y_2O_3$ in $ThO_2$	Low Partial Pressure Electrode of Unknown	Comments
1	Ta, $Ta_2O_5$	90.5	$Ta_5Si_3$ , $Ta_2Si$ , $Ta_2O_5$	Stable EMFs within expected values. Temperature dependence was very strong.
2	Ta, $Ta_2O_5$	90.2	$Ta_5Si_3$ , $Ta_2Si$ , $Ta_2O_5$	Stable EMFs within expected values. Considerable scatter. EMF exhibited a maximum
3	Ta, $Ta_2O_5$		$Ta_5Si_3$ , $Ta_2Si$ , $SiO_2$	Stable EMFs within expected values. Considerable scatter.
4	Ta, $Ta_2O_5$		$Ta_5Si_3$ , $Ta_2Si$ , $SiO_2$	Except for 3 data points in 27 all points fell in a reasonable confidence interval within the expected values. Temperature dependence was strong (23 mv/100C°)
5	Ta, $Ta_2O_5$	90.1	Ta, $Ta_{4.5}Si$	EMFs not within expected values
6	Ta, $Ta_2O_5$	90.1	$SiO_2$ $Ta_{4.5}Si$ , Ta	Stable EMFs obtained
7	Ni, NiO	89.7	$TaSi_2$ , $Ta_5Si_3$ $SiO_2$	The difference between the EMFs for cells (7) and (8) did not equal the EMF for Ni, NiO vs Fe, $Fe_xO$
8	Fe, $Fe_xO$	89.7	$TaSi_2$ , $Ta_5Si_3$ $SiO_2$	

Table II. Partial List of Cells Studied During the Report Period  
(cont.)

Cell No.	Reference Electrode	% Theor. Density of Electrolyte to 7 mol % $Y_2O_3$ in $ThO_2$	Low Partial Pressure Electrode of Unknown	Comments
9	Fe, $Fe_xO$	92	Ta, $Ta_2O_5$	The difference between the EMFs for cells (9) and (10) was substantially equal to the EMF for Ni, NiO vs Fe, $Fe_xO$ . However, the temperature dependence was inconsistent with the expected behavior of the electrolyte.
10	Ni, NiO	90	Ta, $Ta_2O_5$	
11	Ni, NiO	90	C, SiC, $SiO_2$	CO formation appeared to occur
12	Fe, $Fe_xO$	88	TaSi <sub>2</sub>	No reproducible values obtained
13	Ta, $Ta_2O_5$	90	Si, $SiO_2$	EMF maximum was 9 mv at 1000°C. EMF declined to zero.

from brown to white under reducing conditions are readily explained in terms of removal of excess oxygen. Such behavior is common to commercial electrolytes. Radiation induced color changes in commercial materials can be explained in terms of electron trapping. Color changes in electrolytes prepared in this laboratory have not been completely explained.

In an attempt to duplicate the commercial material,  $\text{ThO}_2$  7.25 mol %  $\text{Y}_2\text{O}_3$  was prepared with 0.2 wt %  $\text{SiO}_2$  added as a sintering aid. The resultant pellet was a translucent brownish green. It was very dense and glassy. The presence of  $\text{SiO}_2$  did not impair the electrolytic properties as is indicated by the results given in Table I. The effect of  $\text{SiO}_2$  on the sintering behavior of  $\text{ThO}_2$ - $\text{Y}_2\text{O}_3$  electrolytes will be investigated in the next report period.

## Glass Structure and Growth

The object of this phase of the program is to determine the mechanism of protective film formation by evaluating the structure, composition and growth rate of the oxide film.

In order to clearly establish the intrinsic oxidation behavior of the coating materials, their oxidation is being studied in bulk form. This approach to the coating problem is particularly attractive in that it eliminates the physical problems found in coatings, and also allows the effects of small amounts of additives to be determined. Pure  $\text{TiSi}_2$ , which upon oxidation forms a protective oxide film, is the initial material being considered. When the mechanism of protection for this material is established, the effect on the oxide film of the addition of silicon and  $\text{TaSi}_2$  to the pure  $\text{TiSi}_2$  will be considered.

Wafers of the silicides are prepared by the techniques of powder metallurgy. The initial oxidation studies were carried out in static air in a box-type furnace. Techniques for evaluating the character of the film are being developed using these preliminary specimens. Final oxidation experiments are performed in a tube-type furnace with controlled atmospheres. These studies establish the effect of temperature, oxygen pressure and wafer structure on the character and growth rate of the oxide film. Oxidation mechanisms may then be formulated.

### Analytical Techniques

In earlier X-ray studies, the oxide film was removed from the  $\text{TiSi}_2$  substrate using a chlorine etch at  $700\text{-}800^\circ\text{C}$ . The film was ground and a powder pattern obtained. The purchase of a Norelco diffractometer now allows the analysis to be made without destroying the sample. The oxidized specimen is placed in the sample support holder and the sample scanned. The resulting spectrum shows the  $\text{TiSi}_2$  substrate quite strongly with

smaller oxide peaks also present. Both techniques will continue in use.

### Oxidation Studies

Oxidation runs were made at 300, 600, 800, 1000 and 1200°C. The weight gain data for these runs is shown in Figure 1. The number of samples at each temperature is indicated in parenthesis. An oxygen-argon atmosphere was used with an oxygen partial pressure of 0.2 atm. Sample variation in weight gain, where a number of samples were run, was  $\pm 30\%$ . The runs at 800 and 1200°C were made on samples which had been lapped using automatic polishers while the other samples were lapped by hand.

As indicated in Figure 1, the weight gains were quite low, ranging from 0.015 mg/cm<sup>2</sup> at 300°C for 300 hours to 0.20 mg/cm<sup>2</sup> at 1200°C for 100 hours. In all cases a protective oxide film was formed.

### Character of the Oxide Film

When TiSi<sub>2</sub> is oxidized from 300 to 1300°C there appears to be four structurally distinct oxide films formed. At 300°C where small weight changes are observed, no visible oxide film is formed after 300 hours of oxidation. A few, very small, crystalline, multicolored areas are observed over the sample surface. Whether these are silicide oxidation products or impurity oxides is not known.

At 600°C for 200 hours oxidation, a multicolored, transparent oxide film is formed. In each area, corresponding roughly in size and shape to the substrate grains, one of two or three colors is observed. This color difference may result from a difference either in oxide thickness or refractive index. Microscopic examination of the film reveals no crystalline growth areas. X-ray analysis indicates only the TiSi<sub>2</sub> substrate. Since TiO<sub>2</sub> is found in the X-ray or infrared studies, it is assumed

that the titanium is trapped in the  $\text{SiO}_2$  network. This will be confirmed in later studies.

At  $800^\circ\text{C}$  a transparent oxide film is formed. In this case  $\text{TiO}_2$  crystallization appears to take place at an oxidation time somewhere between 3 and 7 hours. The same phenomenon occurs at  $1000$  and  $1200^\circ\text{C}$ , with crystallization occurring earlier the higher the temperature. At  $1200^\circ\text{C}$  after about 50 hours many small nucleation sites form. In the  $800$  and  $1000^\circ\text{C}$  runs most of the  $\text{TiO}_2$  is segregated into clumps,

In all of the films described above, the oxide film appears to grow via a solid-state reaction. At a temperature around  $1300^\circ\text{C}$ , the structure of the film changes drastically, apparently with a recrystallization of the entire film. The exact temperature, character and extent of protection provided by this film are to be determined.

#### Oxidation Mechanism

One of the most interesting features of the weight-gain data of Figure 1, is the marked deviation of the curves from parabolic behavior. In addition, all curves show a change in slope at some point during the oxidation. Also of interest is the observation that the weight gain at  $800^\circ\text{C}$  is lower than that obtained at  $600^\circ\text{C}$ . Since a large number of samples have not yet been run, the following discussion on possible mechanisms to describe this behavior will be rather general.

Since the oxidation of  $\text{TiSi}_2$  gives rise to a film which appears to be based on an amorphous  $\text{SiO}_2$  network, it is worthwhile to compare the results to those obtained with the oxidation of pure silicon. It is well established (Deal, 1965) that the oxidation of silicon follows a parabolic rate law from  $900$  to  $1200^\circ\text{C}$ , while from  $700$  to  $900^\circ\text{C}$  a combination linear-parabolic law holds with the linear term predominating at the lower

temperature. Also, marker experiments have shown that the oxygen is the diffusing species giving rise to the parabolic mechanism (Pliskin, 1964).

The breaks in the  $\text{TiSi}_2$  oxidation curves, combined with the variation in slope from 2.4 to 6.5 would appear to indicate that a simple bulk diffusion model as in silicon oxidation is unsuitable. When the 300 and 600°C data are plotted on semi-log paper a straight line results. The equations representing these data are

$$T = 300^\circ\text{C} \quad : \quad x = (0.91 \times 10^{-2}) \log t - 8.3 \times 10^{-2}$$

$$T = 600^\circ\text{C} \quad : \quad x = (3.5 \times 10^{-2}) \log t + 2.3 \times 10^{-2}$$

where  $x$  is in  $\text{mg}/\text{cm}^2$  and  $t$  in hours. The 300°C relationship is only valid at times greater than 9 hours. Below this value negative weight changes are predicted. It was experimentally observed that no weight gain occurred at one and three hours. At these low temperatures, the ionic mobility in the lattice is quite small as indicated by the apparent freezing of titanium into the  $\text{SiO}_2$  network. If it is assumed that the surface reaction is still rapid enough (contrary to the case for silicon), a short circuit diffusion model similar to that postulated by Evans (1960) may be suitable. Evans' model does result in a logarithmic relationship. While no experimental evidence is available to support the short circuit idea, there may be microscopic phase separation resulting from the different coordination of silicon and titanium in glasses. This could give rise to lower energy diffusion paths. Methods of determining the extent of phase separation are being investigated.

While the general shape of the curves at 1000 and 1200°C might suggest some form of bulk diffusion and pore closure model, the meaning of the final slope of 3 would be unclear. More

samples will be run to test the validity of the data.

The lower weight gains recorded at 800°C when compared to the 600°C data may be viewed in two ways. Since a different polishing technique was used for the 800°C sample, its lower rate may have been due to a better surface. It is also possible that the effect is due to the character of the film. At 800°C the titanium is apparently rejected from the network and forms crystalline TiO<sub>2</sub>. The resulting purer SiO<sub>2</sub> film is probably more impervious to diffusion, giving a lower rate than for a film with titanium trapped in the network. It is planned to test more samples at these and intermediate temperatures to verify the effect.

## Oxidation Rates and Coating Modifiers

The work described in the previous section was concerned with providing fundamental understanding of glasses formed in silicide oxidation by analyzing the protective and non-protective glasses. At the same time, it is possible to attempt synthesis of protective glasses on the basis of existing principles for glass formation. The technique of manufacturing wafers by powder metallurgy methods lends itself readily to the introduction of modifiers. The composite material may then be evaluated by oxidation rate studies to determine the degree of success.

The experimental method chosen for the production of glasses consists of melting very small quantities (10-20 mg.) in a U - or V - shaped kink in a resistance heated thermocouple wire (Baynton, et al, 1956; Welch, 1954). Simply switching off the heating current results in an extremely rapid quench, since the quantity and surface area of the melt is small compared to air bath environment. Potential crucible materials for melting glass batches are fused silica, alumina, platinum and its alloys, tantalum, and tungsten.

Three basic means of examination and identification will be used. They are metallographic inspection, X-ray diffraction and infra-red spectroscopy.

The experimental procedure for the glass study has gone through a shake-down period with apparent success. The thermocouple serves quite nicely as a sample holder, heater and temperature monitor. The melt droplet is held by capillarity at the point of the V in the thermocouple wire. The couple, Pt 30Rh vs Pt 6Rh will be used up to 1800°C, while Ir 40Rh vs Ir has a 2150°C service limit. The latter couple is severely embrittled by exposure to oxygen, and is much more sensitive to cold junction errors.

Heating is accomplished using a DC source interrupted 60 times a second by a chopper. The chopper is a SPDT relay of the non-bridging type, i. e., it is a break-before-make relay. Contacts are hermetically sealed in a glass capsule filled with high pressure hydrogen, and are mercury wetted. The dwell is approximately equal on the normally open and closed contacts when the coil is driven by 60 H<sub>Z</sub> signal. The contacts must have a 5 amp rating to carry the heating current.

At present the Ta<sub>2</sub>O<sub>5</sub> - SiO<sub>2</sub> binary system is being investigated. A phase diagram will be obtained, while at the same time the glass-forming behavior will be established. Melting is not readily observed in pure silica due to its "flawless" character, unlike other oxides where defects cause very sharp and definitive melting to occur. Of course, the viscosity of silica is also correspondingly higher.

Boron oxide and aluminum oxide will be then used as additives for the binary tantalum-silica system, which is not expected to have an extensive glass-forming region. This choice, follows the concept of replacing two Si<sup>4+</sup> ions with a trivalent-pentavalent ion couple (Grimm and Huppert, 1934, 1937). The integrity and continuity of the silicon-oxygen network should be preserved, along with electroneutrality. If an additive causes a widespread disruption of double-bonded oxygens, then, as is the case with alkali and various other additives, single-bonds will form, destroying the close-knit type network structure as found in pure silica. This undoubtedly affects diffusion of oxygen and cations through the "glass" layer, which is sought to provide oxidation protection for tantalum silicides. An open glass structure would not seem to afford protection for an underlying silicide substrate. Thus, in general, glass-modifier additives should lead to a non-protective oxide scale. Additives of the

intermediate or former type, of which the above-mentioned are included, will have the best chance of aiding protection. The three other candidate additives,  $Ti^{4+}$ ,  $Zr^{4+}$  and  $V^{5+}$ , are of these beneficial types, and will be used in the future.

## Substrate-Coating Interaction and Barriers

The service lifetimes of disilicide coatings are shortened because they interact by diffusion with the metallic substrates to form lower silicides, such as  $Ta_5Si_3$ . The latter are unable to form the protective glassy oxide, presumably because of the simultaneous formation of the substrate metal oxide. Therefore, an understanding of the mechanism of growth of the lower silicide layer and its inhibition is an important approach to increasing the coating life.

In the method used here wafers of the substrate metal and coating material are contacted under pressure at the temperatures of interest. Rates of growth of the intermediate silicides are measured. The same techniques are applied to measure and explain the performance of additive or barrier elements such as titanium and chromium.

In the past six months trial diffusion runs and exploratory results were completed. Eight of the proposed 25 data runs have been completed and the data for the Ta-TaSi<sub>2</sub> couples in these runs analyzed.

The data yield the following result for the growth coefficient,  $\underline{D}$ :

$$\underline{D} = [\bar{D} \Delta C] = (1.9 \times 10^{-4}) e^{-61600/RT}$$

where  $\underline{D}$  is defined by

$$\underline{D} = \frac{(\Delta x)^2}{t} \frac{1}{2} (\rho/M)$$

The parabolic form is assumed to relate zone thickness  $\Delta x$ , to the time for growth  $t$ ;  $(\rho/M)$  is the molar density of the growing phase. This may be compared with the work of Bartlett (1966)

whose result in the same form is:

$$\underline{D} = [\bar{D} \Delta C] = (0.3) e^{-58000/RT}$$

Although the pre-exponential terms are quite different, the values for activation energy compare favorably.

A total of eight trial runs were previously made to develop technique and to obtain samples for exploratory X-ray diffraction work. An effort was made to identify the intermediate phases growing between the various barrier metal wafers and the TaSi<sub>2</sub>. The wafers, after annealing, could be separated at the original interface and the surfaces analyzed. The metal side of the couple showed MSi<sub>2</sub> or M<sub>5</sub>Si<sub>3</sub> or, most commonly, mixtures of the two. The TaSi<sub>2</sub> side showed only Ta<sub>5</sub>Si<sub>3</sub> although it appeared in its two crystallographic forms; that is as a mixture of hexagonal Ta<sub>5</sub>Si<sub>3</sub> and tetragonal Ta<sub>5</sub>Si<sub>3</sub>. Photomicrographs of the various couples were taken to record the appearance of the diffusion zones and to aid in locating the original interface. In most cases there was no difficulty in defining the original interface: it appeared as a series of small holes in a straight line parallel to the phase boundaries. Therefore, marker materials need not be used. It was observed that as the diffusion zones grow, voids accumulated in the Ta<sub>5</sub>Si<sub>3</sub> zone next to the TaSi<sub>2</sub>. This is presumably due to the accumulation of vacancies which accompanies silicon diffusion through the intermediate phases.

Initial analysis of Ta-TaSi<sub>2</sub> data for original boundary position proved very interesting. It can be shown (Kolodney and Graff, 1967a) that:

$$\frac{(\Delta x_2)^2}{(\Delta x_1)^2} = \frac{7 D_{Si}}{3 D_{Si} + 6 D_{Ta}}$$

where  $\Delta x_2$  is the distance of Ta/Ta<sub>5</sub>Si<sub>3</sub> interface and  $\Delta x_1$  the distance of Ta<sub>5</sub>Si<sub>3</sub>/TaSi<sub>2</sub> interface from the original interface. From this the expected ratio is 7/3 if Ta diffusion is negligible or less than 7/3 if Ta diffusion is not. The data, however, show a ratio of more than 7/3. This can be explained in light of the X-ray diffraction work in the Ta-TaSi<sub>2</sub> system. The above ratio can only be expected to hold if the silicon diffusivity is the same on both sides of the original interface. That is to say, the materials are identical. In actuality, two forms of Ta<sub>5</sub>Si<sub>3</sub> grow: the hexagonal form, having higher density and closer packing, and the tetragonal form. This would lead to the hypothesis that diffusion in the tetragonal Ta<sub>5</sub>Si<sub>3</sub> would be higher than in the hexagonal form. In fact there is a mixture of the two forms on both sides of the original interface; but the Ta side contains a considerably higher concentration of the tetragonal Ta<sub>5</sub>Si<sub>3</sub>. Therefore one would expect a higher silicon diffusivity in the  $\Delta x_2$  region than in the  $\Delta x_1$  region. This would account for the high experimental value. It also appears that as diffusion progresses, there is a transition from tetragonal to hexagonal Ta<sub>5</sub>Si<sub>3</sub> and in sufficient time the complete diffusion zone would be homogeneous hexagonal Ta<sub>5</sub>Si<sub>3</sub>. Therefore, as the zone grows in thickness, the ratio  $(\Delta x_2)^2 / (\Delta x_1)^2$  should approach the value of 7/3 if Ta diffusion is neglected. This trend is observed in the data at hand.

Although the raw data for the barrier metals - TaSi<sub>2</sub> couples have been recorded for the first eight runs, they have not yet been analyzed. Nonetheless, it was observed that in each case the diffusion zone in the Ta-TaSi<sub>2</sub> couple was smaller than the zone in the M-TaSi<sub>2</sub> couples. This includes barriers of tungsten, molybdenum, titanium, rhenium, columbium and zirconium.

The diffusion anneals will continue and better techniques

for polishing the couple sandwich will be developed. As of now, some of the barrier metals (Re and Mo, in particular) become extremely embrittled and upon subsequent sectioning, grinding and polishing, the diffusion zones are sometimes separated from the wafers. This makes measurement of the zone impossible, although these data can be salvaged if the sample can be ground down at a later time without again destroying the diffusion zone.

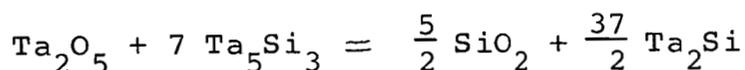
Further X-ray diffraction work will aim at more complete identification of the systems being studied (particularly the Ta-TaSi<sub>2</sub> and Ti-TaSi<sub>2</sub> systems). This will be accomplished by precision grinding through the couple and X-ray diffraction analysis at each step.

### Silicide Reactions

As previously noted, accurate values of the free energies for refractory silicides are not available. Because of this the free energies of silicide reactions have a large probable error and equilibria cannot be accurately determined.

Important information on the systems under study may be obtained as follows: Reactants are mixed in approximately equal volumes, and X-ray spectra before and after heating to reaction temperature are used to identify the reactions that have occurred. Equal volumes are used to make the X-ray peaks detectable.

The first reaction investigated was



The reactants, plus  $\text{SiO}_2$  ( quartz), Si and Ni (.8%) were mixed with binder, made into pellets, presintered, reacted at  $1600^\circ\text{C}$ , and X-rayed. The system  $\text{TiSi}_2\text{-TiO}_2\text{-SiO}_2$  was investigated in the same manner.

No lower silicides were found in the  $\text{Ta}_5\text{Si}_3$  system after heating. The only changes were shifts in the crystal structures of the tri-silicides oxides.

X-ray data on the  $\text{TiSi}_2$  system showed a complete shift to  $\text{Ti}_5\text{Si}_3$  (hexagonal) with no evidence of  $\text{TiSi}_2$ . Investigations of the lower silicides ( $\text{TiSi}$ ,  $\text{Ta}_2\text{Si}$ ) will be undertaken.

## Program for the Next Six-Month Period

### 1. Thermochemical Data:

The completion of EMF measurements for the Ta-Si system is expected during the next six-month period. An investigation of the sintering behavior of  $\text{ThO}_2\text{-Y}_2\text{O}_3$  electrolytes, and the influence of  $\text{SiO}_2$  is also planned. This is expected to lead to a clarification of the color phenomena observed in commercial and laboratory electrolytes.

### 2. Glass Structure and Growth:

The oxidation of pure  $\text{TiSi}_2$  in an oxygen-argon atmosphere will be continued in order to verify and explain the results obtained to date. Additional temperatures and oxygen pressures will be studied. More detailed study of the film using X-ray, infrared and electron microscopy are planned.

### 3. Oxidation Rates and Coating Modifiers:

The Pt 30Rh vs. Pt 6Rh couple will be used for glass studies up to  $1850^\circ\text{C}$ . Above this limit and up to  $2150^\circ\text{C}$  the 60 Ir 40Rh vs Ir couple must be used. However, the experimental apparatus will have to be modified since the junctions between the couple and the extension wires (OFHC COPPER VS. DURAL) only match EMF's up to  $100^\circ\text{C}$ . It might also prove necessary to introduce an inert gas, e.g., argon, to reduce the oxidation of iridium. The binary system  $\text{Ta}_2\text{O}_5\text{-SiO}_2$  will be investigated first. This is to be followed by ternaries with  $\text{Al}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$ .

### 4. Substrate - Coating Interaction and Barriers:

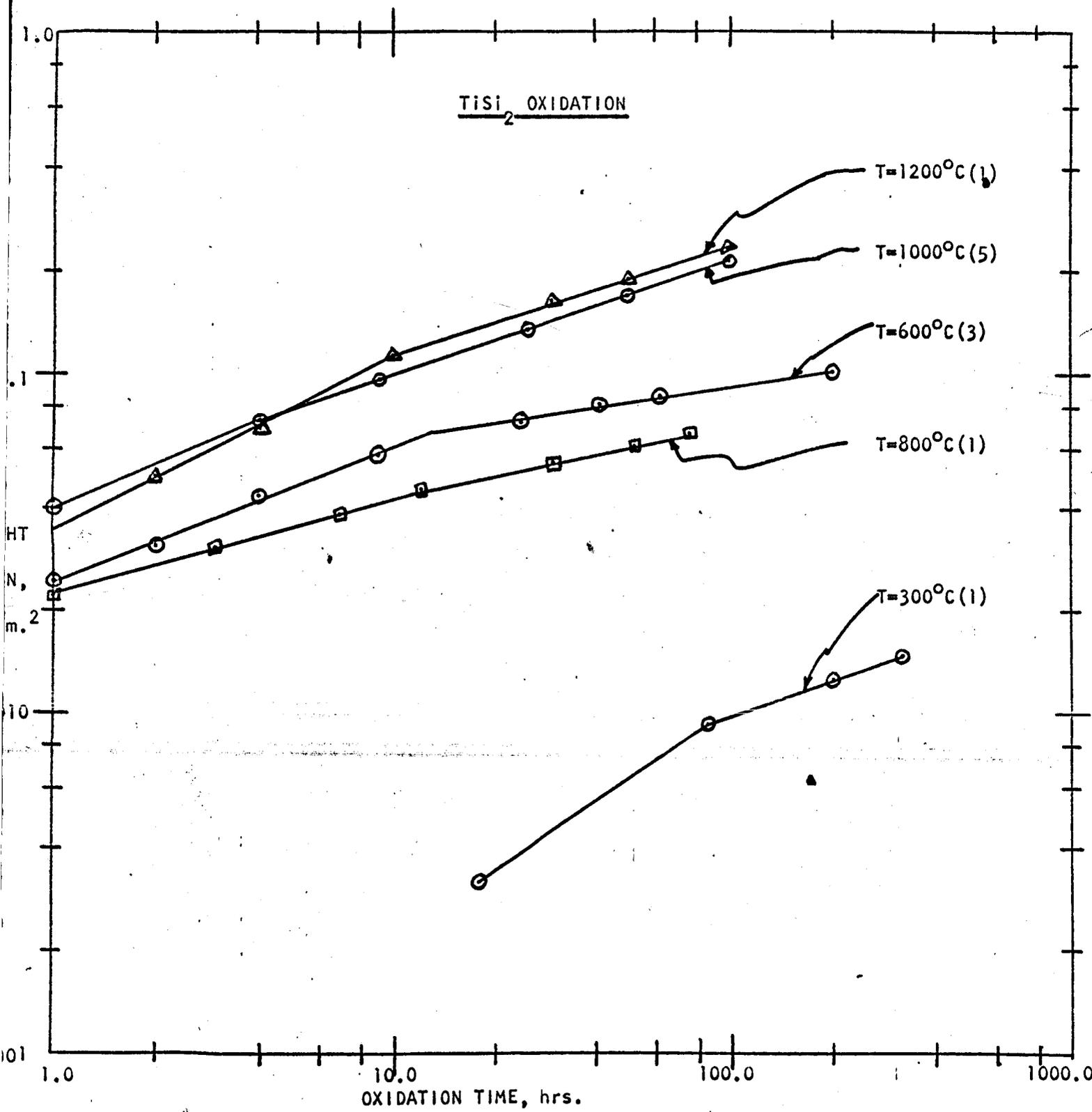
The program of diffusion anneals will be continued. Better polishing techniques for the more brittle materials will be developed. Precision grinding through the diffusion couple with X-ray diffraction analysis at each layer

will be used to identify the phases formed during annealing.

#### 5. Silicide Reactions:

The lower silicides of titanium and tantalum will be studied for stability in the presence of their oxides. The difficult problem of successfully pressing and sintering of silicon powder will be explored so that the oxidation of silicon pellets with small amounts of additives can be investigated.

TiSi<sub>2</sub> OXIDATION



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